

PATENT SPECIFICATION

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(54) MANUFACTURE OF POLYMER DISPERSIONS

(71) We, BADISCHE ANILIN- & SODA - FABRIK AKTIENGESELLSCHAFT, a German Joint Stock Company of 6700 Ludwigshafen, Federal Republic of Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following Statement:—

This invention relates to a process for the manufacture of polymer dispersions of a kind particularly suitable for improving hydraulic binding agents.

It is known to improve the properties of hydraulic binding agents such as gypsum, mortars and concrete by adding aqueous plastics dispersions or by adding dispersible powders obtained from such dispersions. What can be achieved thereby are improved processability of the hydraulic binding agents, improved adhesion of, for example, concrete or mortar to steel or old concrete, reduced permeability to water and other liquids such as oil and petrol, improved resistance to chemicals, for example of concrete roads to salt strewn in winter, and improved flexural and compressive strengths.

In practice, aqueous dispersions based on polyvinyl acetate, vinyl propionate/vinyl chloride copolymers, vinyl acetate/vinyl laurate/vinyl chloride copolymers and styrene/butadiene copolymers are used. The products treated with such dispersions are still unsatisfactory with regard to their overall properties, for example some concretes have high strength properties whilst the cement mixture shows inadequate fluidity, or the cement mixture exhibits adequate fluidity but the resulting concrete shows only slight improvement in its strength properties. Moreover, polyvinyl acetate shows poor resistance to saponification.

Attempts have already been made to improve the properties of hydraulic binders by adding aqueous dispersions of copolymers of

styrene with acrylic esters containing small amounts of polymerized units of α,β - olefinically unsaturated carboxylic acids and/or their amides. However, in the preparation of concrete for example, the use of such additives gives cement mixtures which are thin pastes after only a little has been added but which thicken so rapidly in the concrete mixer that it is necessary to add unusually large amounts of water to maintain processability. The concrete obtained from such mixtures has a longer setting time.

We have now found that the production of polymer dispersions by polymerizing (a) from 40 to 99% by weight based on the total monomer weight of at least one monovinyl or monovinylidene aromatic monomer, (b) from 0.5 to 15% by weight based on the total monomer weight of at least one monomer selected from C_{3-5} α,β -olefinically unsaturated carboxylic acids, their amides, their monoesters with C_{2-4} alkanediols or polyalkylene oxides, and monoolefinically unsaturated sulfonic acids and their water-soluble salts, and (c) from 0 to 59.5% by weight based on the total monomer weight of at least one further copolymerizable olefinically unsaturated monomer, in aqueous emulsion in the presence of an emulsifier and a polymerization initiator, can be carried out with particular advantage by effecting the polymerization in the presence of from 0.001 to 0.5% by weight (based on the total monomer weight) of at least one water-soluble polymer containing carboxamide groups as a further additive component. Aqueous dispersions prepared by this process may be used to particularly good advantage for improving hydraulic binding agents.

In the process of the invention the monomers may be polymerized in conventional manner under the usual conditions of temperature, pressure and concentration. A particularly suitable vinyl aromatic monomer for the process is styrene. Other suitable vinyl or vinylidene

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aromatic monomers are α -methylstyrene and vinyl toluene.

- Particularly suitable monomers (b) are α,β -olefinically unsaturated mono- and dicarboxylic acids of from 3 to 5 carbon atoms and the amides thereof, e.g. acrylic acid, methacrylic acid, crotonic acid, maleic acid, fumaric acid, itaconic acid, acrylamide, methacrylamide, maleic amide, maleic mono-amide and itaconic diamide. Other suitable monomers (b) are monoesters of carboxylic acids of the aforementioned type with C_{2-4} alkanediols, e.g. ethylene glycol, propylene glycol, 1,3-propane diol and butanediol, and monoesters of such carboxylic acids with polyalkylene oxides, especially polyethylene oxides or polypropylene oxides, preferably containing from 2 to 5 and more preferably from 2 to 3 alkylene oxide radicals. Finally, other suitable monomers (b) are monoolefinically unsaturated sulfonic acids such as vinylsulfonic acid and styrenesulfonic acid. In place of acids of this kind, use may be made of their water-soluble salts, for example their sodium or ammonium salts, for the polymerization. In the process of the invention, the monomers (b) are preferably used in quantities ranging from 0.5 to 10%, especially from 1 to 6%, by weight of the total monomers.
- Of the other copolymerizable olefinically unsaturated monomers (c) which may be used in the process of the invention, the esters of C_{3-5} monoolefinically unsaturated carboxylic acids, e.g. mono- and di-carboxylic acids, with alkanols usually containing from 1 to 18 and preferably from 2 to 12 carbon atoms are of particular interest. Specific examples of these comonomers, which are preferably used in amounts ranging from 10 to 50% by weight of the total monomers, are methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, 2-ethylhexyl and lauryl acrylates and methacrylates and dimethyl, diethyl, dibutyl and di-n-propyl maleates. Other suitable monomers (c) are, optionally in admixture with the esters of the kind just mentioned, C_4 or C_5 diolefins such as butadiene and nitriles of α,β -olefinically unsaturated C_{3-5} mono- and di-carboxylic acids, for example acrylonitrile. In some cases it is also advantageous to include as monomers (c) those monomers which enable the polymers to be cross-linked relatively easily, for example butanediol-1,4 diacrylate, butanediol-1,4 methacrylate, hexanediol-1,6 diacrylate, hexanediol-1,6 methacrylate, vinyl acrylate, vinyl methacrylate, diallyl phthalate, divinylbenzene and N-methylolamides of C_{3-5} α,β -olefinically unsaturated mono- and di-carboxylic acids, for example N-methylolacrylamide and N-methylolmethacrylamide, and alkyl ethers and esters of such N-methylolamides, for example N-methoxymethacrylamide, N - n - butoxymethylmethacrylamide and N - acetoxymethacrylamide. Such monomers (c) having

cross-linking activity are generally used in amounts ranging from 0 to 7%, especially from 0.5 to 5%, by weight of the total monomers.

Suitable non-ionic emulsifiers for the process of the invention, which may be used in admixture with ionic, especially anionic, emulsifiers, are in particular oxyalkylation products, especially oxyethylation products, of fatty alcohols, fatty amines, fatty acids and fatty acid amides and of alkyl phenols, these generally containing from 5 to 80 and usually from 5 to 55 moles of added alkylene oxide in each mole. Suitable anionic emulsifiers are, for example, sulfonated oxyalkylation products of the type just mentioned, and also alkyl and aralkyl sulfates or sulfonates, for example lauryl sulfate, and also salts of fatty acids. Particularly suitable polymerization initiators are free radical water-soluble substances, in particular water-soluble peroxides and readily decomposable azo compounds, for example hydrogen peroxide, potassium, sodium and ammonium persulfates, t-butyl hydroperoxide, peracetic acid, azo-diisobutyronitrile and azo-dibutyrylamide. Redox catalysts may also be used in our new process, these consisting of peroxides of the above types and the reducing agents normally used for this purpose, such as ascorbic acid, sodium bisulfide, sodium sulfoxylate and triethanolamine and optionally iron or cobalt salts.

Suitable water-soluble polymers containing carboxamide groups include homopolymers and copolymers of amides of C_{3-6} monoolefinically unsaturated mono- and dicarboxylic acids, in particular acrylamide and methacrylamide, and of vinyl lactams, for example N-vinylpyrrolidone and N-vinyl caprolactam, and also casein. The carboxamide groups may be of the formula $-\text{CONH}_2$ or of the formula $-\text{CONH}-$ or $-\text{CON}<$ forming part of a side chain or of the main chain of the polymer. The copolymers of the above-mentioned polymerizable amides may also contain polymerized units of other olefinically unsaturated monomers, especially monoolefinically unsaturated monomers. Particularly suitable comonomers are C_{3-5} α,β -olefinically unsaturated mono- and di-carboxylic acids and hetero-cyclic monovinyl compounds such as vinyl imidazole and vinyl pyridinium compounds. Up to about 40% of these polymers may consist of polymerized units of monomers which, when polymerized alone, give water-insoluble polymers. However, the amount of such comonomers should be such that at least 1% w/w aqueous solutions can be prepared from the copolymers. Suitable comonomers of this kind are, for example, acrylic and/or methacrylic esters of lower alcohols, for example methyl and ethyl acrylates, and acrylonitrile, vinyl acetate, styrene and vinyl methyl ether. The K values (measured in 1% aqueous solution by the method described by K.

Fikentscher in "Cellulosechemie" Vol. 13 (1932), pp. 58 et seq.) of the polymers are generally between 20 and 150 and in particular between 60 and 150. Particularly suitable are polyvinylpyrrolidone having a K value of from 60 to 100, polyacrylamide having a K value of from 60 to 150, copolymers of from 40 to 60% by weight of acrylamide and from 60 to 40% by weight of methacrylamide and having K values of from 65 to 90, copolymers of from 60 to 80% by weight of acrylamide and/or methacrylamide with from 20 to 40% by weight of vinylpyrrolidone and having K values of from 100 to 140, and copolymers of from 60 to 80 parts of acrylamide and/or methacrylamide with from 18 to 30 parts of vinylpyrrolidone and from 2 to 10 parts of vinyl imidazole and having K values of from 80 to 150.

In the process of the invention, it is possible to use mixtures of a number of water-soluble polymers of olefinically unsaturated amides of the kind mentioned and mixtures of such polymers with casein. The process may be carried out batchwise or continuously. The water-soluble polymers of olefinically unsaturated amides and the casein may be initially present in the aqueous phase and/or added portionwise or continuously to the polymerization mixture during polymerization.

The process of the invention provides aqueous polymer dispersions having a polymer content of generally between 40 and 60% by weight. They may be diluted with water to any desired extent and are particularly suitable for use as additives for improving hydraulic binding agents such as concrete, mortar, lime, gypsum, Sorel cement and in the manufacture of asbestos cement. Where they have appropriate film-forming temperatures or second order transition temperatures, they are also suitable as paint binders, for example for exterior wall paints, as materials for coating plastic sheeting or paper, for coating textiles and leather and, in some cases, as raw materials for adhesives.

The dispersions described in the following Examples are tested for their suitability as improvers for hydraulic binding agents and mixtures thereof with conventional aggregates by the methods laid down in German Standard Specification DIN 1164, the measurement of the flexural and compressive strengths being carried out with prisms which have not been age-hardened in water (as laid down in the DIN Standard) but in air at 20°C and a relative humidity of 65%. The air pore content was determined by the procedures laid down in German Standard Specifications DIN 1045 and 1048. Finally, due to the greater fluidity of the mortar, a lower water/cement ratio was used, for example a ratio of 0.45:1.

To determine the flowability of the mortar, a mixture is prepared in the same manner as for the determination of the flexural and

compressive strengths and is placed in a funnel-shaped mold, the mold is removed and the glass disc supporting the flow specimen is knocked on a base plate 18 times. In the case of very fluid mixtures, the glass is knocked on the base plate less often, this being noted in the results, e.g. 0×27 or 13×26 , etc. The diameter of the specimen after spreading due to the striking is given in cm and is referred to as the spread. The diameter of the mold at its base is 10 cm.

The light permeability values given in the Examples denote the percentage of white light which passes through a 2 cm thick layer of a 0.01% dispersion of the material being tested, taking the light permeability of a 2 cm thick layer of water as 100%.

In the following Examples, the parts are by weight unless otherwise stated. The parts by volume relate to the parts by weight as do liters to kilograms.

EXAMPLE 1.

In a stirred vessel having a capacity of 2,000 parts by volume, a solution of 4 parts of an addition product of 40 moles of ethylene oxide and 1 mole of p-isooctylphenol (=emulsifier I) in 230 parts of water is heated at 78°C under a blanket of nitrogen. 100 parts of a solution of 2.5 parts of potassium persulfate in 122 parts of water are added, and the monomer emulsion is continuously added over the next 90 minutes and the remainder of the potassium persulfate solution is continuously added over the next 2 hours. The monomer emulsion is prepared by emulsifying 280 parts of styrene and 220 parts of n-butyl acrylate in a solution of 16 parts of emulsifier I, 10 parts of a mixture of equal parts of the sodium salt of sulfonated addition products of 8 and 50 moles respectively of ethylene oxide and, in each case, 1 mole of p-isooctylphenol, 2 parts of buten-2-ol-1 as chain stopper, 10 parts of acrylamide and 0.15 parts of a copolymer of 70 parts of methacrylamide, 27.5 parts of vinylpyrrolidone and 2.5 parts of vinyl imidazole having a K value of 136 in 230 parts of water. During polymerization the temperature of the polymerization mixture is kept at 80°C. On completion of the reaction, the temperature is held at 80°C for a further 2 hours and the dispersion is then cooled and adjusted to a pH of from 5 to 6. The resulting dispersion is of low viscosity, smooth and free from specks and coagulate. Its light permeability is 44%.

Examination of dispersion for suitability as improver for cement, mortar and concrete

As stipulated in German Standard Specification DIN 1164, a cement mixture (A) is prepared from

400	parts of standard sand II (particle diameter 0.63 to 1.30 mm),	125
200	parts of standard sand I (particle diameter 0.063 to 0.20 mm),	
200	parts of cement (normal cement con-	

- taining up to 25% by weight of blast furnace slag),
- 40 parts of the dispersion (50%; polymer/cement ratio P/C=0.1)
- 5 70 parts of water (water/cement ratio W/C=0.45) and
- 0.8 parts of a commercial antifoaming agent (NOPCO NDW in admixture with an equal weight of dipentene;
- 10 "NOPCO" is a registered trade mark).
- For the purposes of comparison, a cement mixture (B) is prepared having the same water/cement ratio and the same proportions of sand, cement and antifoaming agent but not
- 15 containing any dispersion. The results of tests
- on the cement mixtures (A) and (B) and the concrete specimens obtained therefrom are given in Table 1 below. Comparison of the data for mixture (A) with the data for mixture (B) shows that the dispersion produced according to the present invention greatly increases the fluidity of cement mortar and moldings made from said cement mortar show distinct improvements as regards their flexural and compressive strengths. The setting time is only slightly prolonged when using the dispersion of the invention. Cement floors made using the dispersion prepared in Example 1 may be walked on without spoiling after a setting time of 16 hours.
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- 30

TABLE 1

	Mixture (A)	Mixture (B)
Spread: 5 min after mixing	6×27	10.5
30 min after mixing	10×28	10.5
Flexural strength after air-conditioned storage for 28 days	110 kg/cm ²	64 kg/cm ²
Compressive strength after air-conditioned storage for 28 days	404 kg/cm ²	384 kg/cm ²
Air pore content	3.5%	7.5%
Setting commences after	3 hrs 16 min	3 hrs 40 min
Setting complete after	5 hrs 44 min	4 hrs 35 min

EXAMPLES 2 to 4.

- Polymerization is carried out as described in Example 1 except that the copolymer of methacrylamide, vinylpyrrolidone and vinyl imidazole is replaced by 0.15 part of polyvinylpyrrolidone (K value 90) (Example 2) or by 0.15 part of a copolymer of 30 parts of methacrylamide and 70 parts of vinylpyrrolidone and having a K value of 110 (Example 3) or by 0.15 part of a copolymer
- 35
- 40
- of 50 parts of methacrylamide and 50 parts of acrylamide and having a K value of 73 (Example 4). There are then obtained dispersions which are also smooth and virtually free from specks and coagulate and have a light permeability of from 35 to 36% and 47% respectively. They are examined for suitability for improving hydraulic binding agents in the manner described in Example 1, and the results are given in Table 2 below:
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- 50

TABLE 2

Example	Spread		Flexural strength (kg/cm ²)	Compressive strength (kg/cm ²)	Air pore content (%)	Setting commences		Setting complete	
	5 min (cm)	30 min (cm)				hrs	min	hrs	min
2	23	23	93	396	5.4	3	23	6	44
3	23	26	105	385	5.2	3	8	6	43
4	27	12×28	108	406	4.7	3	25	6	44

EXAMPLE 5.

In a polymerization vessel fitted with a reflux condenser, a solution of 1.1 parts of a 35% solution of the sodium salt of a sulfonated addition product of 25 moles of ethylene oxide and 1 mole of p-isooctylphenol (emulsifier II) and 0.5 part of potassium persulfate in 205 parts of water is heated to 78°C and a monomer emulsion which has been adjusted to pH 6—7 with calcium hydroxide solution is continuously added over 2 hours, polymerization being effected at 85°C. The monomer emulsion is prepared by emulsifying 392 parts of styrene in a solution of 8 parts of acrylic acid, 40 parts of emulsifier II, 1.6 parts of potassium persulfate and 0.04 part of a copolymer of 70 parts of methacrylamide, 27.5 parts of vinylpyrrolidone and 2.5 parts of vinyl imidazole and having a K value of 110 in 406 parts of water. On completion of the addition of the monomer emulsion, the temperature of the polymerization mixture is maintained at 85°C for a further hour, after which the mixture is cooled and the resulting dispersion is adjusted to pH 7 by adding calcium hydroxide solution. There is obtained a thin dispersion having a solids content of 40.2%. Its light permeability is 24%. The dispersion is suitable for improving the properties of hydraulic binding agents.

Examination of dispersion as additive for cement mixtures

A cement mixture is prepared in the manner described in Example 1 but using the present dispersion, the polymer/cement ratio being 0.05. The spread of the mixture is 22 cm after 5 minutes and 20 cm after 30 minutes. Setting commences after 2 hours 38 minutes and is complete after 3 hours 26 minutes at room temperature, these values being substantially the same as those obtained for a cement mixture not containing the said dispersion. The specimens prepared from the cement/water/dispersion/sand mixture are not age-hardened at room temperature but for 6 hours at 80°C, testing thereof then being effected at 40°C. Under these conditions the flexural strength is 51 kg/cm², the compressive strength is 270 kg/cm² and the air pore content is 3.4%. Specimens prepared from a cement mixture having the same water/cement ratio and prepared under the same age-hardening conditions but not containing the polymeric additive show, when tested under the same test conditions, a flexural strength of only 43 kg/cm², a compressive strength of only 230 kg/cm² and an air pore content of 3.2%.

WHAT WE CLAIM IS:—

1. A process for the manufacture of a poly-

mer dispersion of polymerizing (a) from 40 to 99% by weight based on the total monomer weight of at least one monovinyl or monovinylidene aromatic monomer, (b) from 0.5 to 15% by weight based on the total monomer weight of at least one monomer selected from C₃₋₅ α,β-olefinically unsaturated carboxylic acids, their amides, their monoesters with C₂₋₄ alkanediols or polyalkylene oxides, and mono-olefinically unsaturated sulfonic acids and their water-soluble salts, and (c) from 0 to 59.5% by weight based on the total monomer weight of at least one further copolymerisable olefinically unsaturated monomer, in aqueous emulsion in the presence of an emulsifier and a polymerization initiator, wherein polymerization is carried out in the presence of from 0.001 to 0.5% by weight, based on the total monomer weight, of at least one water-soluble polymer containing carboxamide groups as a further additive component.

2. A process as claimed in claim 1 wherein monomer component (a) is selected from styrene, α-methylstyrene and vinyl toluene.

3. A process as claimed in claim 1 or 2 wherein monomer component (b) is selected from acrylic acid, methacrylic acid, crotonic acid, maleic acid, fumaric acid, itaconic acid, acrylamide, methacrylamide, maleamide, maleic acid monoamide and itaconic diamide.

4. A process as claimed in any of claims 1 to 3 wherein monomer component (c) is present in an amount of from 10 to 50% by weight and is selected from esters of C₃₋₅ mono-olefinically unsaturated mono- and di-carboxylic acids with alkanols containing from 1 to 18 carbon atoms.

5. A process as claimed in any of claims 1 to 4 wherein the or each water-soluble polymer containing carboxamide groups contains the carboxamide groups in side chains.

6. A process as claimed in any of claims 1 to 5 wherein the or each water-soluble polymer containing carboxamide groups is selected from homopolymers and copolymers of vinyl lactams and amides of C₃₋₆ monoolefinically unsaturated mono- and di-carboxylic acids, and casein.

7. A process as claimed in claim 6 wherein the or each water-soluble polymer containing carboxamide groups has a K value of from 60 to 150.

8. A process as claimed in claim 1 substantially as hereinbefore described or exemplified.

9. A polymer dispersion when produced by a process as claimed in any of claims 1 to 8.

10. A composition comprising a hydraulic binding agent and a polymer dispersion as claimed in claim 9.

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